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# Investigation of the chemical structure of secondary combustion in laminar fuel-rich CH<sub>4</sub> and CH<sub>4</sub>-NH<sub>3</sub> flames

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## Abstract

Secondary combustion is central to the rich-burn/quick-mix/lean-burn (RQL) scheme proposed for stable and low-emission combustion of methane-ammonia blends. However, the secondary stage has received relatively little attention, and the formation and reaction characteristics of secondary combustion remain insufficiently understood. In this study, we investigate the structure of laminar premixed fuel-rich methane and methane-ammonia flames and the properties of their secondary front, using a specially designed burner with controllable ventilation conditions. Flame photographs and global chemiluminescence of OH\*, CH\*, C<sub>2</sub>\* and NH<sub>2</sub>\* are used to characterise the overall flame behaviour. Hyperspectral imaging (HSI), combined with CO<sub>2</sub>\* background-emission removal and Tikhonov-regularisation reconstruction, is then employed to obtain spatial distributions of OH\*, CH\*, C<sub>2</sub>\*, NH<sub>2</sub>\*, and H<sub>2</sub>O. The results show that the shape and chemiluminescent signatures of the secondary front in fuel-rich laminar flames exhibit under- and over-ventilated behaviour governed by the flow rate of air ventilation (21% O<sub>2</sub> vol%), whereas when the total flow is fixed and O<sub>2</sub> vol% is varied this behaviour weakens and the secondary front changes more monotonically. Spatial reconstructions reveal that CH\* and C<sub>2</sub>\* are concentrated at the primary premixed front and are almost absent at the secondary front, whereas the secondary front is dominated by OH\* and CO<sub>2</sub>\*. NH<sub>2</sub>\* are present only at the primary front and the intermediate region between two fronts. Subsequently, the bluish luminosity of the secondary flame front is predominantly contributed by CO<sub>2</sub>\*. Coupled with kinetic calculations, this study confirms that oxidation of H<sub>2</sub> and moist-CO play critical roles in the secondary combustion of methane and methane-ammonia flames up to 40% in ammonia fraction, rather than hydrocarbons or unburnt primary fuels. These findings provide new insights into the formation of secondary combustion under fuel-rich conditions and demonstrate that the employed diagnostic methods are well suited to study the characteristics of the RQL combustion scheme.

**Novelty and significance:** By applying hyperspectral imaging (HSI) combined with Tikhonov-regularisation reconstruction and background-emission elimination to spontaneous flame emission, this work achieves, for the first time, a species-resolved characterisation of the secondary combustion zone in fuel-rich CH<sub>4</sub> and CH<sub>4</sub>-NH<sub>3</sub> flames. The significance lies mainly in two aspects. First, this study experimentally and numerically demonstrates that the luminous secondary front is governed by OH\* and CO<sub>2</sub>\*, while CH\*, C<sub>2</sub>\* and NH<sub>2</sub>\* remain confined to the primary or intermediate regions, establishing the secondary combustion as CO/H<sub>2</sub> oxidation rather than an extension of hydrocarbon or ammonia burning. This provides mechanistic guidance for stabilising and optimising ammonia-containing-fuel-based RQL systems. Second, the HSI-based diagnostic method provides full spectra at each spatial location, achieving combined spatial and spectral resolution and thereby offering a species-resolved tool applicable to investigations of a wide range of stable flames.

**Keywords:** Methane/ammonia flame; Flame chemiluminescence; Secondary combustion; Hyperspectral imaging; Combustion diagnostics

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## 1. Introduction

In recent years, the efficient utilisation of low-carbon fuels has become increasingly important to meet global carbon-emission targets. However, concerns have been raised regarding their use, particularly ammonia- or hydrogen-blended fuels and methane-based fuels, including high NO<sub>x</sub> emissions from ammonia, fuel slip, and combustion stability issues arising from fuel compatibility. To address these challenges, the Rich-burn, Quick-mixing, Lean-burn (RQL) combustion scheme has attracted considerable interest [1]. As a typical staged combustion strategy, it comprises a primary fuel-rich stage with an equivalence ratio ( $\Phi$ ) of up to 1.8 followed by a secondary combustion process downstream [2]. Despite its benefits in stability, fuel flexibility, and NO<sub>x</sub> control, optimisation of the RQL scheme remains challenging because of the complex interactions between the primary fuel-rich flame and the downstream secondary combustion zone [3]. Understanding the mechanisms and flame properties of secondary combustion process is therefore essential for further optimisation of RQL systems.

A detailed investigation of the overall structure of a typical fuel-rich premixed flame can offer insights into the primary and secondary stages of the RQL scheme. At the primary flame front, combustion proceeds under oxygen-deficient conditions, leading to incomplete oxidation and the formation of substantial amounts of intermediate species together with residual unburnt fuel [4]. In fuel rich methane flames, the main intermediates are mainly CO, H<sub>2</sub> and C<sub>2</sub> species, with their relative fraction controlled by the premixed equivalence ratio ( $\Phi$ ) [4–6]. In ammonia flames, the primary stage can yield N<sub>2</sub>, H<sub>2</sub> and other nitrogen-containing species via incomplete oxidation and decomposition [7,8]. When hydrocarbons are blended with ammonia, the intermediate compositions become more complex owing to additional reaction pathways that involve hydrocarbon, nitrogenous, and their cross-linked species and radicals. [7,9,10]. These variations in the kinetic and intermediate composition are strongly related to pressure, ammonia fractions and  $\Phi$ , and can in turn impact the flame structure, temperature, lift-off length, NO/CO distributions and species fraction [6,7,9,10]. Accordingly, characterising secondary combustion in fuel-rich methane and methane-ammonia flames can inform the optimisation of staged strategies such as RQL.

The secondary combustion of a fuel-rich premixed mixture is essentially a diffusion flame fuelled by combustible intermediate species. This connects directly to the extensive body of work on diffusion flames. Burke-Schumann theory states that diffusion flame shape and length vary with ventilation conditions [11–13], while experimental and theoretical studies show that the co-flow conditions affect CH distributions, residence time, flame length and lift-off limits [14–16]. The flame flicking frequency and amplitude also scale with the air co-flow velocity for both diffusion flame and partially premixed flame [17–19]. Varying the co-flow oxygen concentration or composition can also strongly affect the flame structure, dynamics and reaction behaviour of both hydrocarbon and ammonia-blended hydrocarbon flames [20–25]. For instance, a higher oxygen level increases the flame temperature and NO formation, but reduces the flame length, lift-off height, recirculation region size located at the potential core, and the mean particulate size if soot is present. Specifically, in syngas (CO/H<sub>2</sub>), C<sub>2</sub>-fuel, and NH<sub>3</sub>/H<sub>2</sub> diffusion flames, which are relevant to key intermediates formed during incomplete methane and methane/ammonia combustion, changes in the properties of co-flow significantly impact the diffusion rates and reaction pathways, and thus reshape the flame front and reaction zones [10,21,26,27].

Although some studies have examined partially premixed flames under varying co-flow conditions [18,28–30], these flames are usually unconfined. In such configurations, the unburnt fuel and its intermediates are diluted and consumed in the ambient air, and hence the secondary-combustion environment is difficult to control. Meanwhile, the co-flow is usually applied in close proximity to the burner exit [12,19]. However, far less attention has been paid to secondary combustion in fuel-rich premixed flames under well-controlled ventilation in confined geometries, especially when both ventilation rate and co-flow oxygen concentration are systematically varied.

To evaluate and characterise the combustion behaviour, flame chemiluminescence is widely utilised [31–35]. In hydrocarbon flames, OH\*, CH\*, C<sub>2</sub>\* and CO<sub>2</sub>\* are the most well-known chemiluminescence signatures, which can serve as important markers for heat release and flame front location [31,36,37]. In ammonia-containing flames, OH\*, NO\*, NH\* and NH<sub>2</sub>\* also become important [34,35]. Some recent studies on laminar flames have employed hyperspectral imaging (HSI) for reliable spectral and spatial reconstruction of flame properties and demonstrated its suitability for methane-premixed, ammonia-ethylene inverse-diffusion flames and biomass combustion [38–41].

To further understand the secondary combustion process, this study experimentally investigates the effects of ambient conditions on the flame properties of fuel-rich methane and methane-ammonia premixed flames up to an ammonia fraction of 0.4 that methane chemistry dominates. A specially designed burner was utilised to modulate the secondary combustion using a ventilation stream with varied ventilation air flow rates and oxygen concentrations. Hyperspectral imaging (HSI), combined with Tikhonov-regularisation reconstruction algorithms was used to retrieve spatial distributions of CO<sub>2</sub>\*, NH<sub>2</sub>\* and H<sub>2</sub>O through their chemiluminescence and spontaneous emissions. Subsequently, a linear background-elimination process was applied to isolate OH\*, CH\* and C<sub>2</sub>\* spatial distributions from CO<sub>2</sub>\*. Together with the flame photos and global emission intensities of OH\*, CH\* and C<sub>2</sub>\* obtained by photomultiplier tubes (PMT), the effects of ventilation on the burning behaviours and flame structures were experimentally assessed. Kinetic calculations were conducted to further elucidate the combustion behaviours and the reaction mechanisms involved in the secondary combustion. The insights gained from this study can deepen the understanding of the secondary combustion process, and potentially serve as a foundation for control strategies and optimisation of the RQL combustion schemes that employ methane-based and ammonia-containing low-carbon fuels.

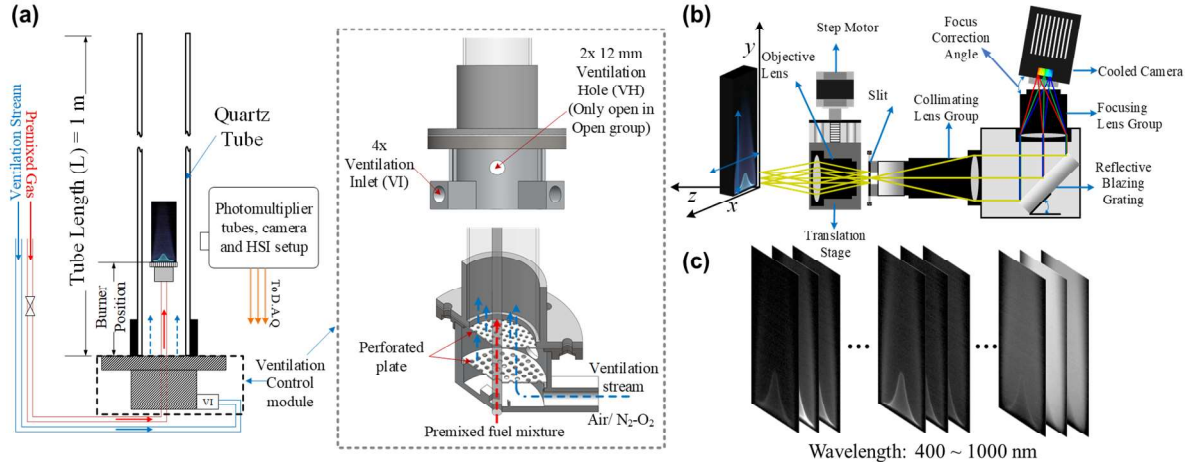


Fig. 1 (a): A schematic figure of the experiment arrangement, (b) Hyperspectral imaging (HSI) system, (c): examples of HSI image datacube

## 2. Methodology

### 2.1. Experimental setup

A schematic of the experimental setup is shown in Fig. 1(a). The specially designed burner for modulating the secondary combustion atmosphere consists of a vertically placed quartz tube combustion chamber (1 m in length and 40 mm in inner diameter) and a base-mounted enclosure ventilation module to control the ventilation condition. Four evenly spaced ventilation inlets (VIs) and two ventilation holes (VHs) were perforated at the module. The ventilation inlets supply the adjustable ventilation stream, with a 90° spacing between adjacent inlets. Two perforated plates were installed to ensure a stable and uniform ventilation flow into the tube. A nozzle with a honeycomb flame holder was placed at the lower quarter of the

tube, where the premixed laminar flame was located. The nozzle has an exit diameter of 30 mm. All flow rates in this study are volumetric flow rates in standard litres per minute. Two Aalborg GFC17 flow controllers were used to control the methane and air flow rate with an accuracy of 0.05% for methane and 0.1% for air. The fuel flow rate ( $\dot{V}_{fuel}$ ) was set at 0.9 L/min to maintain an approximately constant total fuel molar flow rate while varying the blend ratio. The premixed equivalence ratio ( $\Phi$ ) was varied from 0.9 to 1.6 by varying the air flow rate, so that primary-stage chemistry and intermediate formation are controlled via fuel composition and  $\Phi$  while maintaining a constant heat release when varying  $\Phi$ . These conditions correspond to Reynolds numbers ranging from 276 to 462 for methane cases and from 230 to 410 for methane-ammonia cases, confirming laminar flow across all test conditions in this study. Two types of ventilation stream, air and N<sub>2</sub>-O<sub>2</sub> mixture, were introduced to respectively

investigate the effects of air flow rate ( $\dot{V}_{air}$ ) and oxygen concentration ( $O_2$  vol%), thereby controlling the secondary-stage oxidation environment through ventilation rate and oxidiser composition. The ventilation air flowrate was controlled by using an Aalborg GFC37 flow controller with an accuracy of 0.1%, and the flowrates of  $N_2$ ,  $O_2$  for the  $N_2$ - $O_2$  mixture were respectively controlled by two Aalborg GFC17 controllers with accuracies of 0.07%. The closed group in this study, all the ventilation inlets and holes were blocked to stop fresh air intake. For the controlled ventilation conditions, the ventilation air flow ( $\dot{V}_{air}$ ) was set to different values ranging from 1 to 10 L/min to investigate the characteristics of the flame under different ventilation conditions to investigate the effect of ventilation strength on secondary front, while keeping the ventilation holes closed. For the  $N_2$ - $O_2$  stream, the  $O_2$  vol% was ranging from 0% to 40% to cover the oxygen-lean and oxygen-rich condition and thus investigate the influence of oxygen concentration on the secondary combustion process. The total flowrate of  $N_2$ - $O_2$  stream ( $\dot{V}_{vent}$ ) was set to 5 L/min to ensure a similar flow and minimise ventilation induced flow effects and convective heat transfer differences on the flame. A National Instruments cDAQ-9178 chassis was utilised to control the flow controllers and acquire the Photomultiplier tubes (PMT) data using NI-9264 and NI-9220 modules, respectively.

In order to provide an intuitively illustration the changes in flame structure, the flame photographs were captured by a Canon 6D DSLR camera with a lens of 105 mm focal length and an f/4 aperture. Four PMTs were utilised to capture the global  $OH^*$ ,  $CH^*$ ,  $C_2^*$  and  $NH_2^*$  chemiluminescence signals. Each PMT assembly consists of a Hamamatsu R3896 PMT and a Hamamatsu C8991 high-voltage power unit. The obtained current signals were converted to voltage and amplified by the corresponding transimpedance amplifier with the same gain of  $10^6$ . The chemiluminescence of  $OH^*$ ,  $CH^*$ ,  $C_2^*$  and  $NH_2^*$  were acquired by applying 308 nm, 431 nm, 516 nm and 633 nm bandpass filters (all with 10 nm bandwidth) with the transmission rates of 57%, 88.7%, 89% and 90%, respectively. A 1-to-4 optical fibre was utilised for light transmission. A Galilean configuration comprising a biconvex and a biconcave lens was placed before the fibre receiving head to collimate the light, thereby removing spatial information at the receiver and minimising variability among the signals acquired by the PMTs. Meanwhile, a beam-shaping optical assembly, comprising a plano-convex lens, an adjustable iris, and a band-pass filter, was mounted in front of each PMT to collimate the light from the fibre and to regulate the light level. This ensured that the light falls only on the PMT active area, thereby mitigating potential stray light and measurement noise.

A custom-developed reflective hyperspectral imaging system was utilised to capture the hyperspectral imaging data for the spectral reconstruction of both the methane and methane-ammonia flames, as shown in Fig. 1 (b). The original configuration using a transmission grating has been reported in our previous study, and the detailed concepts are given accordingly [39]. In the present study, this system was optimised by employing a 25 mm, 900 lines/mm reflective blazing grating to enhance optical efficiency. To verify the measurements from the custom-developed HSI system, a SOC710VP commercial HSI system was further utilised for comparison and verification during the development of this custom HSI system, and for obtaining the spectra and  $H_2O$  distributions. The custom-developed HSI system was utilised to reconstruct  $CH^*$ ,  $C_2^*$ ,  $NH_2^*$ ,  $CO_2^*$ , with emission bands within 400-1000 nm. The exposure time for HSI systems was set to 500 ms. In addition to the HSI system, an Andor iStar UV-ICCD camera was also utilised for reconstruction of  $OH^*$  with an exposure time of 500 ms, and three bandpass filters (300 nm, 308 nm, and 320 nm) were installed to enable background-emission elimination.

## 2.2. Kinetic calculations

The kinetic calculations for the cases under varying  $O_2$  vol% conditions were performed using Chemkin-Pro. The GRI-Mech 3.0

mechanism and CEU-NH3-1.1 were utilised for methane and methane-ammonia combustion, respectively. They were extended by incorporating the excited-state radical sub-mechanisms from Konnov's works [7,8], together with the associated transport and thermodynamic data. The calculations were conducted using the opposed-flow flame model considering the Soret effect and multicomponent transport. The absolute and relative tolerance were set to  $10^{-9}$  and  $10^{-4}$ , respectively. The inlet velocity of premixed fuel and oxidiser streams were both set to 0.5 m/s, and the separation distance between the inlets was set to 20 mm. This corresponds to a low strain rate of  $50 s^{-1}$  at the stagnation plane, which lies in the low-moderate range typically utilised for kinetic studies [42,43]. This relatively low strain rate keeps the flame weakly stretched and quasi-steady, ensuring that chemical kinetics and diffusive transport dominate, and minimise the stretch-induced effects on the high-strain extinction and quenching in excited radicals.

## 2.3. Image processing methods

The flame images recorded by the HSI system represent the line-of-sight integrated chemiluminescence intensity. To recover the spatial distribution of chemiluminescence in the flame, Tikhonov regularisation technique is employed, which can effectively reduce the reconstruction errors caused by instrument noise [44]. For an axisymmetric flame, the flame radius,  $r$ , at height  $z = z_0$  is divided into  $N$  concentric and equally spaced annular elements. According to the radiation imaging model [44], the relationship between the spatial distribution of chemiluminescence and its projection  $I$  on the camera can be written as:

$$I_\lambda = A H_\lambda$$

where  $I_\lambda$  and  $H_\lambda$  denote the matrices of projection and spatial distribution of chemiluminescence at wavelength of  $\lambda$ , respectively, and  $A$  is the system matrix determined by the imaging setup. The spatial distribution  $H_\lambda$  can be reconstructed using Tikhonov regularisation, expressed as:

$$H_\lambda = (A^T A + \alpha D^T D)^{-1} A^T I_\lambda$$

where  $\alpha$  is the Tikhonov regularisation parameter.

The broad-band background emission contributed by some species, such as  $CO_2^*$  and  $NH_2^*$  [8,45,46], together with soot blackbody radiation, can overlap the targeted chemiluminescence across the UV-visible range, potentially compromising the flame-structure characterisation. Hence, the spatial and spectral reconstruction of the flame, together with background-emission eliminations, is essential for accurate analysis of the secondary combustion behaviour and for identifying the dominant fuel species driving that process. Recent studies have proven that suppressing background emission contributed by soot and  $CO_2^*$  through linear or integrated approaches based on HSI spectral reconstruction, together with Tikhonov-regularised spatial reconstruction, is effective for a laminar diffusion flame [38,40]. Accordingly, combining HSI with spectral-spatial reconstruction with background-emission eliminations can provide key insights into the flame structure and properties of secondary combustion of methane and methane-ammonia flames. In addition, colour images reconstructed from the HSI data are provided for intuitive illustration, following the colour reconstruction procedure reported in our previous study [47].

In this study, the linear background-emission eliminations, previously employed in study [38], was applied for obtaining the background-emission-free spatial distributions of  $OH^*$ ,  $CH^*$  and  $C_2^*$ , as schematically illustrated in Fig. 2. Three spatially reconstructed images at different wavelengths were selected for each excited radical, with one centred on the main emission peak ( $\lambda$ ) and other two at neighbouring off-line wavelengths ( $\lambda-s$  and  $\lambda+s$ ). The images at  $\lambda-s$  and  $\lambda+s$  were utilised to estimate, for every pixel, a linear background by interpolating the intensities between these two off-line bands. The interpolated background field was then subtracted from the image at  $\lambda$  to give the corrected chemiluminescence intensity image  $I_c$ , which

represents the spatial distribution of the target radical with the background emission removed.

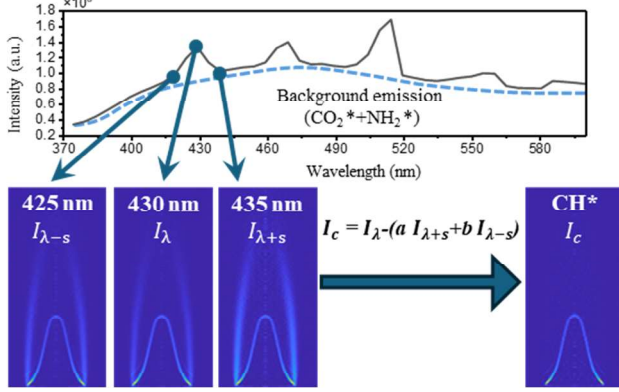


Fig. 2 Schematic of linear background elimination method.

### 3. Results and Discussion

#### 3.1. General flame behaviours

##### 3.1.1. Methane flame

Fig. 3 and Fig. 4 display respectively the effects of  $\dot{V}_{\text{air}}$  and  $\text{O}_2$  vol% on the overall shape of methane flames at  $\Phi = 0.9$  and  $\Phi = 1.5$ .  $\Phi = 0.9$  is included as a lean reference case to show that secondary combustion is negligible under fuel-lean or near-stoichiometric condition, whereas  $\Phi = 1.5$  represents a fuel-rich case with pronounced secondary combustion. These figures also report the global chemiluminescence intensities of  $\text{OH}^*$ ,  $\text{CH}^*$  and  $\text{C}_2^*$ , which are used here to reflect changes in overall combustion behaviour. Generally, variations in both  $\dot{V}_{\text{air}}$  and  $\text{O}_2$  vol% barely influence the flame in terms of flame shape for  $\Phi = 0.9$  and global chemiluminescence for the cases of within near-stoichiometric and fuel-lean region, consistent with the expectation of complete combustion in the primary combustion process under lean and near-stoichiometric conditions.

##### ➤ Varying $\dot{V}_{\text{air}}$

For the rich mixture of  $\Phi = 1.5$ , the inner cone (primary flame front) is almost insensitive to the  $\dot{V}_{\text{air}}$ , whereas the outer cone (secondary

flame front) responds strongly. The secondary front does not exist when  $\dot{V}_{\text{air}} = 0$  L/min. As  $\dot{V}_{\text{air}}$  increases, a short secondary front forms near the flame root, grows and gradually tilts towards the primary front, as shown in Fig. 3 (a). The flame shape then becomes stable when  $\dot{V}_{\text{air}}$  is greater than 5 L/min. The evolution of the secondary front with  $\dot{V}_{\text{air}}$  shows noticeable similarity to the Burke-Schumann flame structure [12]. The  $\text{OH}^*$ ,  $\text{CH}^*$  and  $\text{C}_2^*$  chemiluminescence intensities (Fig. 3 (b) ~ (d)) exhibit nonlinear trends with increasing  $\Phi$  regardless of the value of  $\dot{V}_{\text{air}}$ , consistent with previous studies [33,36,47–49]. Across near-stoichiometric conditions ( $0.9 < \Phi < 1.05$ ), these intensities remain weakly dependent on  $\Phi$ . For  $\Phi > 1.05$ , the intensities increase with  $\dot{V}_{\text{air}}$  and then plateau around 5 L/min, as illustrated by the  $\Phi = 1.5$  cases in Fig. 3 (e). Together, the flame-shape evolution and chemiluminescence trends support a classification into under-ventilated ( $\dot{V}_{\text{air}} < 5$  L/min), and over-ventilated ( $\dot{V}_{\text{air}} > 5$  L/min) conditions in the present configuration, which is consistent with the diffusion-controlled nature of the secondary combustion.

##### ➤ Varying $\text{O}_2$ vol%

Varying  $\text{O}_2$  vol% of the ventilation stream produces changes similar to those caused by  $\dot{V}_{\text{air}}$  at  $\Phi = 1.5$ . The primary front remains nearly unchanged, whereas the secondary flame front disappears under 0%  $\text{O}_2$  vol%, and then reappears, tilting towards the primary front as  $\text{O}_2$  vol% increases, as shown in Fig. 4 (a). The results of  $\text{OH}^*$ ,  $\text{CH}^*$  and  $\text{C}_2^*$  to  $\text{O}_2$  vol% also show weak sensitivity below  $\Phi = 1.05$ , but monotonic increase with  $\text{O}_2$  vol% up to 40% in richer mixtures, as illustrated in Fig. 4 (b) to (e). These observations trend conforms to the existing studies of diffusion flames [24,27], and supports the interpretation that the secondary front is diffusion-flame-like in nature. Meanwhile, under oxygen-rich conditions, the secondary flame front becomes more luminous while appearing less saturated, a feature that is not observed in  $\dot{V}_{\text{air}}$  cases. Together with the  $\text{CH}^*$  and  $\text{C}_2^*$ , this is best explained by a strengthened  $\text{CO}_2^*$  continuum since increases in  $\text{CH}^*$  and  $\text{C}_2^*$  are less likely to reduce colour contrast of the flame appearance. Notably, as  $\text{O}_2$  vol% increases, the trend of  $\text{OH}^*$  changes from decreasing to increasing with  $\Phi$  in fuel-rich range, while trends of  $\text{CH}^*$  and  $\text{C}_2^*$  shift upwards without an obvious change in trend. This indicates that secondary combustion more likely involves and associates with  $\text{OH}^*$  production, which is more closely related to the reactions of  $\text{H}_2$  and  $\text{CO}$ , rather than  $\text{CH}^*$  and  $\text{C}_2^*$  production which is related to reactions of hydrocarbons.

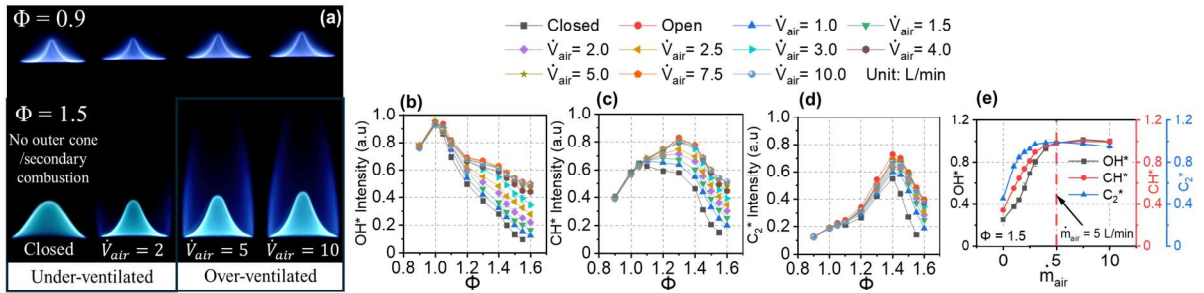


Fig. 3 (a) Flame photos of  $\Phi = 0.9$  and  $1.5$  and, (b)  $\text{OH}^*$ , (c)  $\text{CH}^*$ , (d)  $\text{C}_2^*$  chemiluminescence intensities under varying  $\dot{V}_{\text{air}}$ . (e)  $\text{OH}^*$ ,  $\text{CH}^*$ ,  $\text{C}_2^*$  intensities changes with  $\dot{V}_{\text{air}}$  under  $\Phi = 1.5$ .

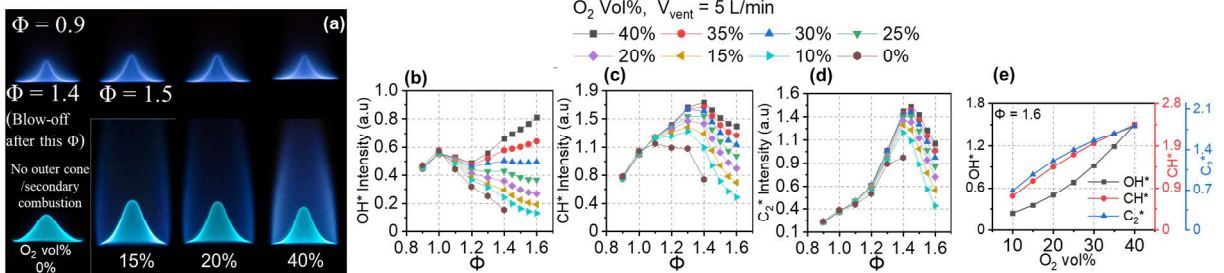


Fig. 4 (a) Flame photos of  $\Phi = 0.9$  and  $1.5$  and, (b)  $\text{OH}^*$ , (c)  $\text{CH}^*$ , (d)  $\text{C}_2^*$  chemiluminescence intensities under varying  $\text{O}_2$  vol%. (e)  $\text{OH}^*$ ,  $\text{CH}^*$ ,  $\text{C}_2^*$  intensities changes with  $\text{O}_2$  vol% under  $\Phi = 1.5$ . Note that the flame blow-off occurs at  $\Phi = 1.5$  under 0%  $\text{O}_2$  vol%, thus  $\Phi = 1.4$  was selected for the demonstration in flame photos.

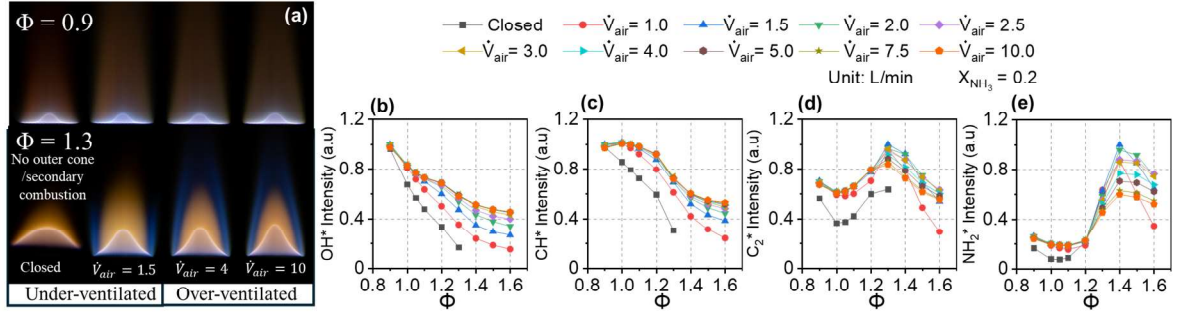


Fig. 5 (a) Flame photos of  $\Phi = 0.9$  and  $1.5$  and, (b)  $OH^*$ , (c)  $CH^*$ , (d)  $C_2^*$  (e)  $NH_2^*$  chemiluminescence intensities with  $X_{NH_3} = 0.2$  under varying  $\dot{V}_{air}$ .

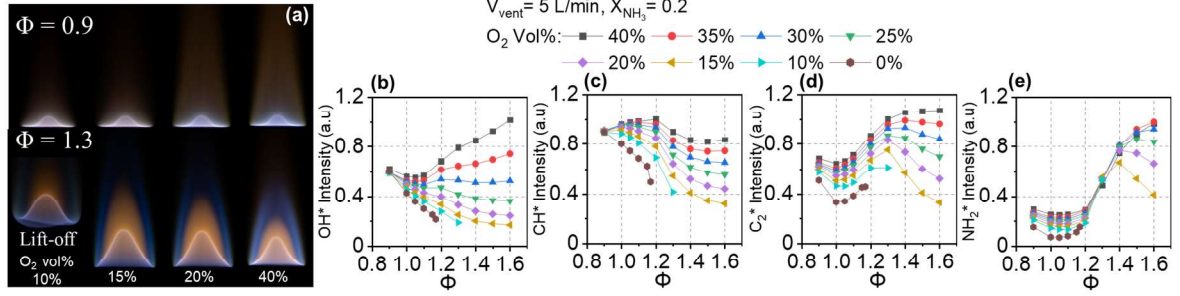


Fig. 6 (a) Flame photos of  $\Phi = 0.9$  and  $1.5$  and, (b)  $OH^*$ , (c)  $CH^*$ , (d)  $C_2^*$  (e)  $NH_2^*$  chemiluminescence intensities with  $X_{NH_3} = 0.2$  under varying  $O_2$  vol%. Note that the flame blow-off occurs when  $O_2$  vol% below 10%, thus 10%  $O_2$  vol% was selected for the demonstration.

### 3.1.2. Methane-Ammonia flame

In methane-ammonia flames with ammonia fraction ( $X_{NH_3}$ ) of 0.2, the overall response of flame shape and chemiluminescence to  $\dot{V}_{air}$  and  $O_2$  vol% is broadly consistent with the pure-methane cases, as shown in Fig. 5 and Fig. 6. Specifically, when  $\Phi = 0.9$ , the flames are almost insensitive to  $\dot{V}_{air}$  and  $O_2$  vol% changes. For fuel-rich flames, a critical  $\dot{V}_{air} \approx 4$  L/min separates under- and over-ventilated regimes, and increase in  $O_2$  vol% makes the secondary front respond continuously in tilting towards primary front and become more luminous while appearing less saturated. Ammonia addition, however, also introduces distinct features. At  $\Phi = 1.3$ , a clear three-region structure is formed, consisting of a primary front, an intense yellow intermediate region and a pale bluish secondary front that envelopes the intermediate region and is separated from it by a dark gap, indicating distinct combustion zones. The yellowish chemiluminescence is believed to originate from  $NH_2^*$ , which exhibits a continuum emission with its peak intensity mainly distributed within 'yellow-orange' portion of the spectrum [35]. The spectral characterisation of these regions will be discussed in the flame reconstruction section.

The intensities of  $OH^*$ ,  $CH^*$ ,  $C_2^*$  and  $NH_2^*$  are also insensitive to  $\dot{V}_{air}$  when the flame is in near stoichiometric conditions. But in fuel-rich condition,  $OH^*$  and  $CH^*$  increase with  $\dot{V}_{air}$  up to 4 L/min and then plateau, consistent with the ventilation-based conditions categorisation. In contrast,  $C_2^*$  and  $NH_2^*$  show an increase-then-decrease with  $\dot{V}_{air}$ .  $NH_2^*$  remains nearly constant up to  $\Phi = 1.2$  and then increases, consistent with the observed broadening of the intermediate region for  $\Phi > 1.2$ , and supporting the attribution of  $NH_2^*$  to the intermediate region. When  $O_2$  vol% is varied,  $OH^*$ ,  $CH^*$ ,  $C_2^*$  and  $NH_2^*$  increases monotonically with oxygen enrichment in fuel-rich flames. The changes in  $OH^*$  trend with  $O_2$  vol% from decrease to increase in fuel-rich region persist, further indicates the important role of  $OH^*$  related reactions in methane-ammonia secondary combustion process.

### 3.1.3. Summary from the general flame behaviours

Combining the methane and methane-ammonia flame results, these observations suggest a fact in which the secondary flame front under varying ventilation conditions similarly to a Burke-Schumann

diffusion flame [12] [50]. To provide overall oxygen availability context, we introduce a global equivalence ratio,  $\Phi_G$ , defined from the total fuel flow rate and the total oxidiser supply. Under sufficiently high ventilation airflow or high  $O_2$  vol%,  $\Phi_G$  can fall below unity, whereas at lower ventilation some conditions remain globally fuel rich. However, the under-ventilated and over-ventilated classification discussed above does not show a one-to-one correspondence with  $\Phi_G$ . In particular, some under-ventilated cases can still have  $\Phi_G < 1$ . The secondary front is diffusion controlled and can be interpreted, in the Burke-Schumann theory, as the locus of locally stoichiometric mixing governed primarily by the local transport and mixing field rather than by a single global value of  $\Phi_G$ , although  $\Phi_G$  provides useful overall measurement of the oxygen availability. Consistent with this, the primary flame front geometry is weakly coupled to the surrounding oxidiser conditions, as supported by the negligible changes in the primary front when varying  $O_2$  vol%.

It is worth noting that the general trend of  $OH^*$  with  $\Phi$  in fuel-rich range for both methane and methane-ammonia flame, changes from decreasing to increasing as  $O_2$  vol% rises, whereas significant changes in general trend of  $CH^*$  and  $C_2^*$  is absent. Hence, a hypothesis can be proposed that the secondary combustion of methane and methane-ammonia flame more strongly involves  $OH^*$  formation, whereas  $CH^*$  and  $C_2^*$  are less dominant. However, since  $OH^*$  emits predominantly in the UV range, it cannot explain the visible luminosity of the secondary front. The brightness of the secondary zone must therefore be controlled mainly by other emitters, such as  $CO_2^*$  continuum. This motivates the subsequent hyperspectral reconstructions to resolve the spatial contributions of each radical.

### 3.2. HSI-based flame reconstruction

To further understand and explain the current findings and to characterise the secondary combustion, spatial and spectral reconstructions were carried out. The spatial distributions of  $OH^*$ ,  $CH^*$  and  $C_2^*$  were reconstructed after background-emission elimination. For  $CO_2^*$  and  $NH_2^*$ , reconstructions were performed using their emissions at 450 nm and 633 nm, respectively, to minimise interference from overlapping bands by other radicals. Additionally, the spatial distribution of  $H_2O$  was reconstructed based on its infrared radiation by integrating the intensity from 920 to 930 nm, which

corresponds to one of the strongest near-infrared radiations of superheated  $\text{H}_2\text{O}$  vapour [46]. To complement the spatial reconstructions, location-specific emission spectra were obtained at the primary and secondary flame fronts and in the intermediate region at selected representative positions. Unless otherwise stated, Points A, B and C are defined using objective criteria based on the reconstructed intensity profiles. Point A refers to the primary flame front and is defined as the local maximum (peak) of the reconstructed intensity profile associated with the primary front. Point B for the methane flames and  $\Phi = 0.9$  cases denotes the region immediately downstream of the primary front and is defined as the first location downstream of Point A at which the reconstructed  $\text{CH}^*$  intensity decreases to the background level. For the fuel-rich methane-ammonia flame, Point B refers to the intermediate region. Point C refers to the secondary flame front and is defined in the same manner as Point A, as the local maximum (peak) of the reconstructed intensity profile corresponding to the secondary-front within the secondary reaction zone. In fuel-lean flames, Point C is instead used to denote the downstream product zone.

### 3.2.1. Methane flame

For  $\Phi = 0.9$ , as shown in Fig. 7, the reconstruction results are consistent with the flame photos and global chemiluminescence measurements.  $\text{OH}^*$ ,  $\text{CH}^*$ ,  $\text{C}_2^*$  and  $\text{CO}_2^*$  show no noticeable change in their spatial distributions under different ventilation conditions, indicating similar combustion behaviours. The spatial distribution of

$\text{H}_2\text{O}$ , which is located downstream of the primary flame front, exhibits changes in its inclination when ventilation  $\dot{V}_{\text{air}}$  is increased (Fig. 7 (a)), but remains insensitive to  $\text{O}_2$  vol% changes (Fig. 7 (b)). This indicates that the  $\text{H}_2\text{O}$  distribution is governed mainly by the flow field rather than oxygen enrichment, consistent with complete combustion at the flame front.

The location-specific spectra further show that  $\text{OH}^*$ ,  $\text{CH}^*$ ,  $\text{C}_2^*$  appear exclusively at the primary flame front, as indicated by point A in Fig. 7 (c).  $\text{CO}_2^*$  also peaks there but extends slightly downstream as indicated by spectrum at point B, in which  $\text{CH}^*$  and  $\text{C}_2^*$  peaks are barely identifiable. Its intensity decreases rapidly downstream of the primary flame front, and becomes negligible at point C. This indicates that  $\text{CO}_2^*$  is primarily present within the flame front where the rapid reactions take place. In contrast,  $\text{H}_2\text{O}$  shows approximately uniform emission over a broad region downstream of the flame front and is not dominant at the flame front, as shown by the spectrum at Point A. This indicates that superheated  $\text{H}_2\text{O}$  vapour is concentrated in the product zone of the flame [46]. The different distributions of  $\text{H}_2\text{O}$  and other excited radicals result from the different emission mechanisms.  $\text{H}_2\text{O}$  radiation originates from the rotational-vibrational transition of its molecule rather than the radiative relaxation of the excited radicals, meaning that its radiation is less related to the reaction process. Given the low sensitivity of the  $\Phi = 0.9$  flame to ventilation in the present results, the following discussion therefore focuses on fuel rich conditions.

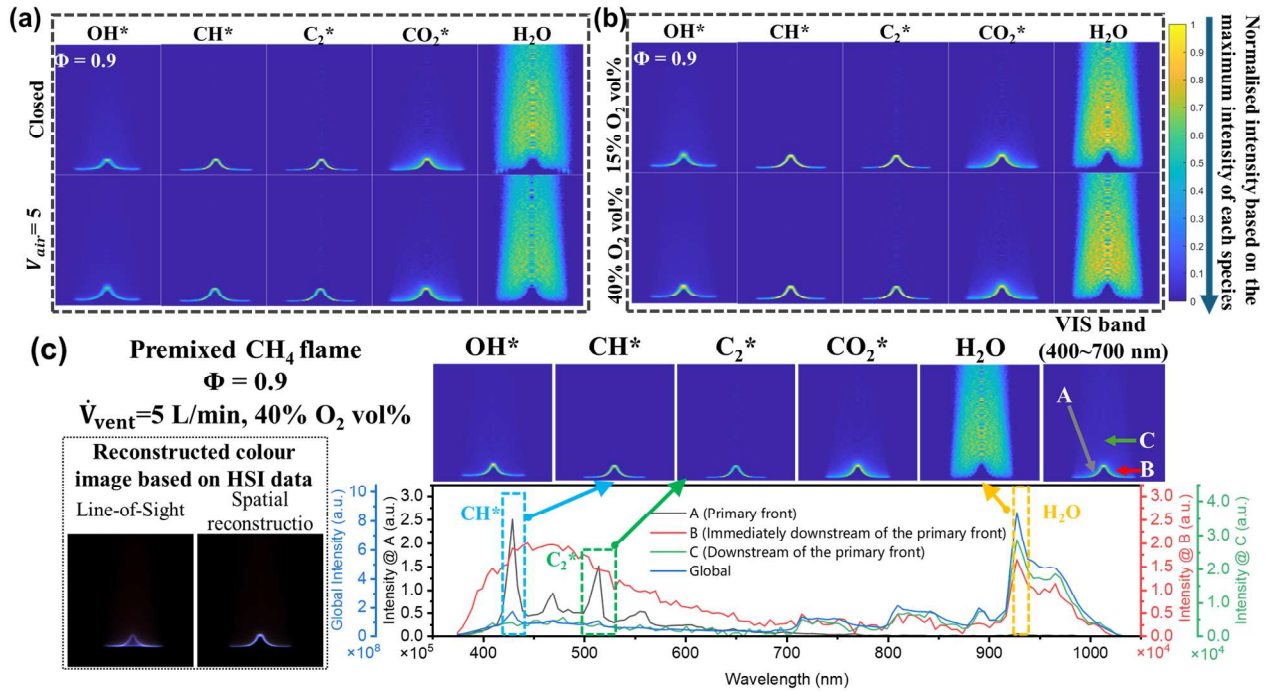


Fig. 7 Comparison of key species spatial distributions in  $\text{CH}_4$  flame under varying ventilation (a)  $\dot{V}_{\text{air}}$  and (b)  $\text{O}_2$  vol% at  $\Phi = 0.9$ . (c): Reconstruction results and corresponding spectra at different locations for the flame at  $\Phi = 0.9$ , and 40%  $\text{O}_2$  vol%.

As  $\Phi$  increases to the fuel-rich range, the spatial distributions of these key species become sensitive to both ventilation  $\dot{V}_{\text{air}}$  and  $\text{O}_2$  vol%. At  $\Phi = 1.2$ ,  $\text{OH}^*$ ,  $\text{CH}^*$ ,  $\text{C}_2^*$  are confined to the primary flame front with the absence of secondary flame front when no ventilation is introduced, as shown in upper part of Fig. 8 (a) and (b).  $\text{CO}_2^*$  shows a similar pattern but extends slightly into the region immediately downstream of the primary flame front. In contrast,  $\text{H}_2\text{O}$  radiation is observable downstream of the primary front without a pronounced peak even at the primary flame front. The reconstructed species distributions indicate no subsequent secondary combustion after the primary premixed combustion.

Introducing oxygen-containing ventilation stream (air and  $\text{N}_2\text{-O}_2$  mixtures) produces a distinct secondary flame front. Generally,

increasing  $\text{O}_2$  vol% markedly strengthens  $\text{OH}^*$ ,  $\text{CO}_2^*$  and  $\text{H}_2\text{O}$  at the secondary flame front, as shown in the middle and bottom rows of the right panel of Fig. 8 (b), whereas varying  $\dot{V}_{\text{air}}$  mainly changes the inclination of the secondary flame front with only modest intensity changes, as shown in the Fig. 8 (a). The distribution of  $\text{H}_2\text{O}$  extends throughout the post-primary-combustion region, indicating  $\text{H}_2\text{O}$  is produced initially from the primary combustion process. Its presence at the secondary flame front demonstrates its participation in secondary combustion. The intensified local peak at the secondary front also evidences its further formation. Under 40%  $\text{O}_2$  vol%, the intensities of  $\text{H}_2\text{O}$  at the secondary flame front becomes stronger than that at the primary front, showing that oxygen enrichment substantially promotes  $\text{H}_2\text{O}$  formation during the secondary combustion process.

Interestingly,  $\text{OH}^*$ ,  $\text{CH}^*$ ,  $\text{C}_2^*$  and  $\text{CO}_2^*$  exhibit distinct spatial distributions in fuel-rich flames. As shown in Fig. 8,  $\text{CH}^*$  and  $\text{C}_2^*$ , as key excited radicals involved in hydrocarbon combustion, are confined to the primary flame front but are absent at the secondary flame front. In contrast,  $\text{OH}^*$  and  $\text{CO}_2^*$  appear at both flame fronts. For the 40%  $\text{O}_2$  vol% case, which most strongly promotes secondary combustion (Fig. 8 (c)), the location-specific emission spectra show

clear differences between the two fronts. At point A (primary front),  $\text{CH}^*$  and  $\text{C}_2^*$  peaks are present and the  $\text{CO}_2^*$  continuum is clearly identifiable, whereas at point C (secondary front) the spectrum is predominantly contributed by  $\text{CO}_2^*$  continuum without  $\text{CH}^*$  or  $\text{C}_2^*$  peaks. This distinction suggests hydrocarbon-related excited radicals are largely confined to the primary combustion process, with limited involvement at the secondary flame front.

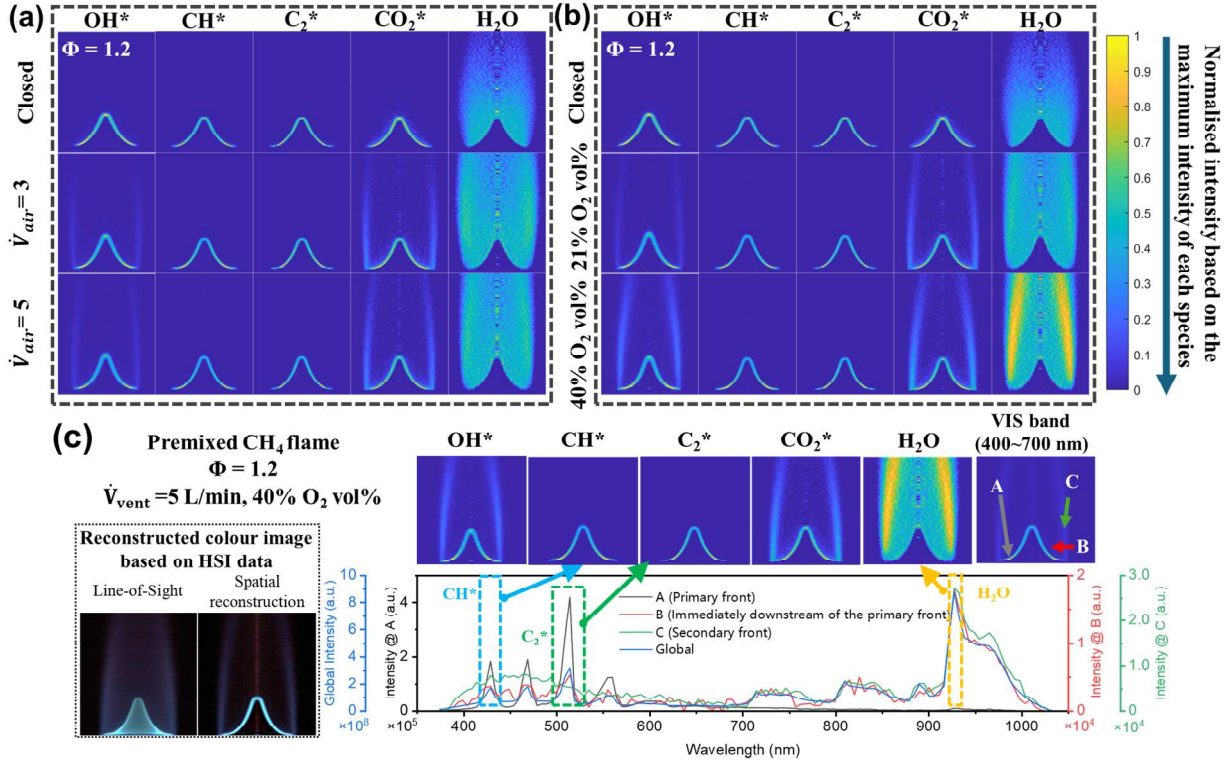


Fig. 8 Comparison of key species spatial distributions in  $\text{CH}_4$  flame under varying ventilation (a)  $\dot{V}_{\text{air}}$  and (b)  $\text{O}_2$  vol% at  $\Phi = 1.2$ . (c): Reconstruction results and corresponding spectra at different locations for the flame at  $\Phi = 1.2$ , and 40%  $\text{O}_2$  vol%.

### 3.2.2. Methane-ammonia flame

#### ➤ Effect of $\dot{V}_{\text{air}}$ and $\text{O}_2$ vol%

Ammonia addition modifies the flame behaviour because nitrogen participates actively in oxidation, thereby altering the spectral properties of the flame relative to the pure methane cases. For comparisons across different  $\Phi$  and ventilation conditions, the discussion focuses on cases with  $X_{\text{NH}_3} = 20\%$  to enable consistency with previous chemiluminescence and flame-photograph results. Under  $\Phi = 0.9$ , as shown in the Fig. 9 (a), the reconstructed spatial distributions of the radicals remain similar to the methane flame. While,  $\text{H}_2\text{O}$  shows a clear peak at the primary flame front, indicating increased  $\text{H}_2\text{O}$  production during the primary combustion process. This is reasonable because for one mole  $\text{O}_2$ ,  $\text{NH}_3$  oxidation yields twice as much  $\text{H}_2\text{O}$  as  $\text{CH}_4$  oxidation, and thus  $\text{NH}_3$  participation increases  $\text{H}_2\text{O}$  production.

Meanwhile,  $\text{NH}_2^*$  shows sensitivity to  $\dot{V}_{\text{air}}$  and  $\text{O}_2$  vol% in both distribution and intensity at  $\Phi = 0.9$ . In closed cases, there is no typical separated front of its distribution from the primary flame front, as shown in upper part of Fig. 9 and Fig. 10 (a). With ventilation, a spatially separated secondary  $\text{NH}_2^*$  distribution zone from primary front with a noticeable local peak appears (lower part of Fig. 9 and Fig. 10 (a)). This explains the positive correlation between  $\text{NH}_2^*$  intensity and  $\text{O}_2$  vol% observed in PMT measurements under near-stoichiometric conditions and supports attribution of the yellowish ‘tail’ to  $\text{NH}_2^*$ , as a higher  $\text{O}_2$  vol% promotes  $\text{NH}_2^*$  formation in the secondary zone. Taken together with the complete absence of  $\text{CH}^*$  and  $\text{C}_2^*$  downstream of the flame front, and the lower reactivity of ammonia compared with methane, these results indicate the presence

of ammonia slip at the primary flame front, which feeds a secondary combustion process governed by ammonia under the near-stoichiometric conditions. In addition, the spectra shown in Fig. 11 (a) shows that the background emission exhibits different spectrum compared to pure-methane cases. Specifically, the background emission peaks at around 450 nm for the pure-methane case at point B (Fig. 8 (c)), which is contributed by  $\text{CO}_2^*$ , while it peaks at around 500-700 nm when ammonia is present (Fig. 11 (c)), which is caused by the combination of  $\text{CO}_2^*$  and  $\text{NH}_2^*$  continuum [35,51].

As  $\Phi$  increases to 1.2, the spatial distributions of  $\text{OH}^*$ ,  $\text{CH}^*$ ,  $\text{C}_2^*$  and  $\text{CO}_2^*$  responding to  $\dot{V}_{\text{air}}$  and  $\text{O}_2$  vol% remain similar to those in the methane flame, as shown in Fig. 9 (b) and Fig. 10 (b). Notably, when a secondary combustion flame front exists,  $\text{CH}^*$  and  $\text{C}_2^*$  remain confined to the primary flame front and are absent at the secondary flame front, as shown in Fig. 11 (b) and the spectra at points A and C. This supports the conclusion that hydrocarbon-related excited radicals are negligible at the secondary front when ammonia is introduced.  $\text{OH}^*$  and  $\text{CO}_2^*$  appear at both flame fronts, with their intensities at the secondary flame front increasing with  $\text{O}_2$  vol% rises, most clearly for  $\text{OH}^*$ .  $\text{NH}_2^*$  can be detected at the primary front and in the intermediate region, while it is nearly negligible at the secondary front. The  $\text{H}_2\text{O}$  distribution follows the pattern seen under  $\Phi = 0.9$ , showing a sharp peak at the primary flame front and thus indicating elevated  $\text{H}_2\text{O}$  production during the primary combustion process under fuel-rich conditions compared to methane cases. Downstream of the primary front, the  $\text{H}_2\text{O}$  levels remain nearly uniform until the secondary flame front, where a secondary peak arises, indicating further  $\text{H}_2\text{O}$  production during the secondary combustion process.

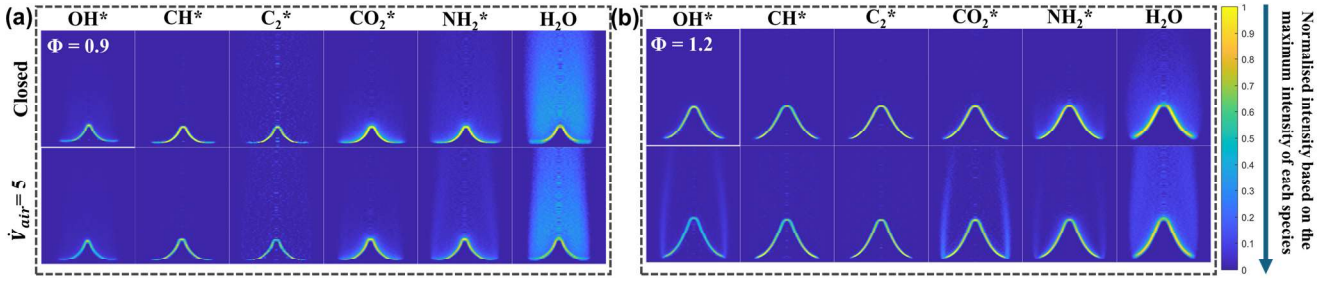


Fig. 9 Comparison of key species spatial distributions in the  $\text{CH}_4\text{-NH}_3$  flame with  $X_{\text{NH}_3} = 0.2$  under varying ventilation  $\dot{V}_{\text{air}}$  at (a)  $\Phi = 0.9$  and (b) 1.2.

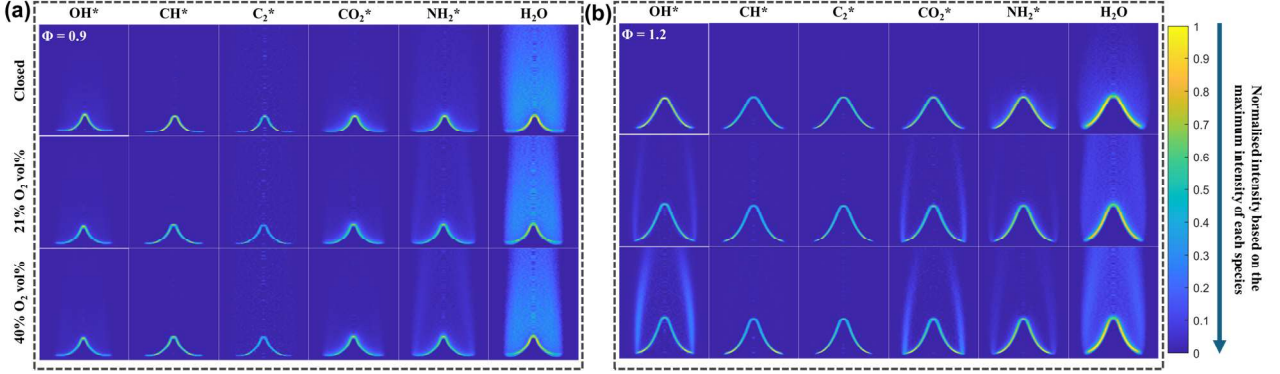


Fig. 10 Comparison of key species spatial distributions in  $\text{CH}_4\text{-NH}_3$  flame with  $X_{\text{NH}_3} = 0.2$  under varying ventilation  $\text{O}_2$  vol% at (a)  $\Phi = 0.9$  and (b) 1.2.

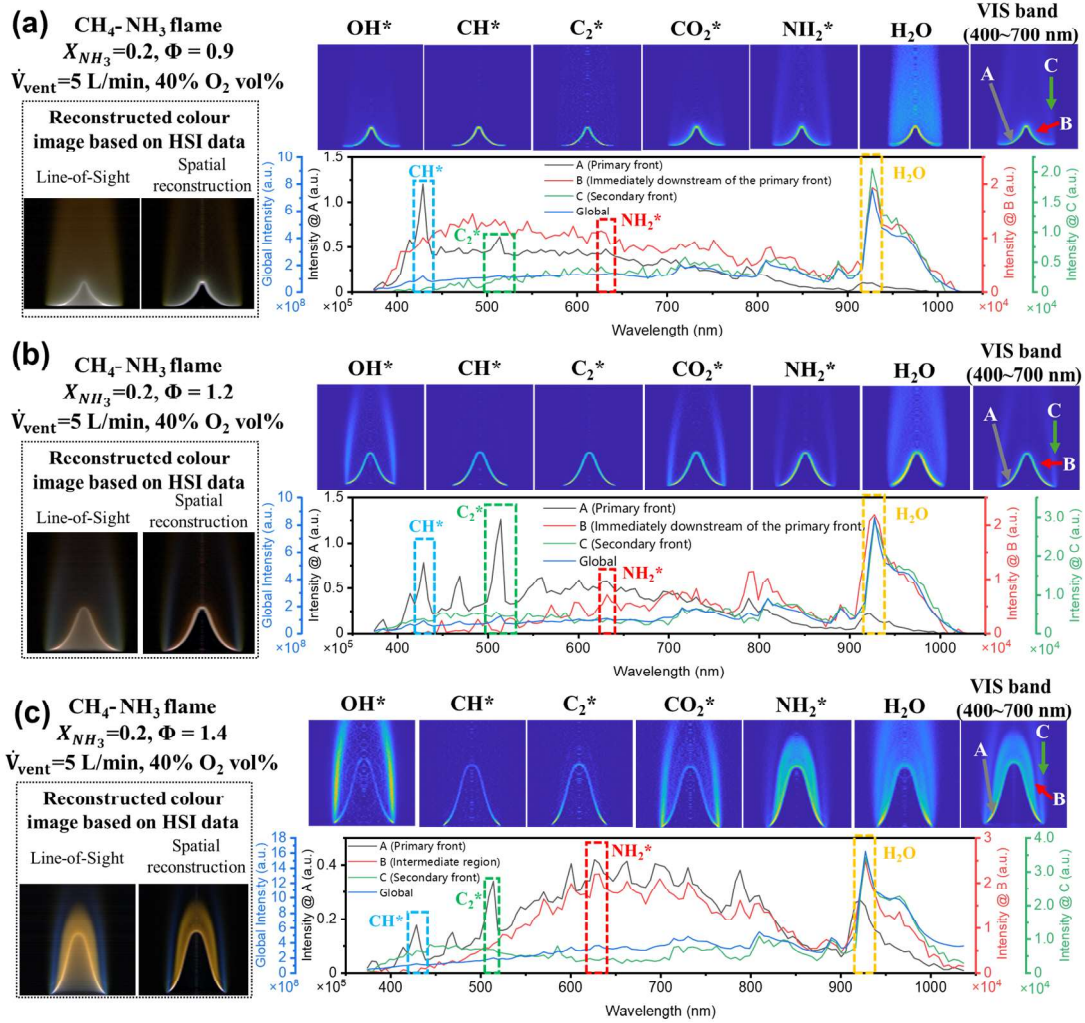


Fig. 11 Reconstruction results and corresponding spectra at different locations for the flame at  $\Phi =$  (a): 0.9, (b): 1.2, and (c) 1.4 with 40%  $\text{O}_2$  vol%.

At  $\Phi = 1.4$ , a clear gap between the intermediate region and the secondary front can be identified from the  $\text{NH}_2^*$  distribution, whereas the intermediate region remains directly adjacent to the primary front,

consistent with the observation from the flame photos. Within this region, no other chemiluminescence can be observed, and no noticeable  $\text{H}_2\text{O}$  production can be traced, indicating the absence of

intense oxidation. Based on this, this region likely corresponds to a broadened reaction zone resulting from ammonia's low reactivity and the associated Damköhler number (Da). Consistent with this interpretation, the intermediate region is broader at  $\Phi = 1.4$  (Fig. 11 (c)) than at  $\Phi = 1.2$  (Fig. 11 (b)). Meanwhile, the spectra of the primary flame front and intermediate region in the 500–800 nm range for the methane-ammonia flame show higher intensity than for methane flame. At  $\Phi = 1.4$ , the point A spectrum in Fig. 11 (c) shows that the peak intensity in this band can exceed the  $\text{CH}^*$  and  $\text{C}_2^*$  peaks, which is mainly attributable to the  $\text{NH}_2^*$  continuum [35]. However, the spectrum of the secondary flame front (point C) exhibits a typical  $\text{CO}_2^*$  continuum spectrum, whose peak intensity at around 450 nm, and a markedly reduced  $\text{NH}_2^*$  contribution. Since  $\text{NH}_2^*$  is related to  $\text{NH}_3$  combustion rather than thermal decomposition, these features suggest that  $\text{NH}_3$  is mostly oxidised across the primary combustion process and the intermediate region, with limited involvement in the secondary combustion process.

#### ➤ Effects of ammonia fraction

Beyond the effects of ventilation  $\text{O}_2$  vol% and  $\dot{V}_{\text{air}}$ , changes in  $X_{\text{NH}_3}$  also affect species distributions and the flame structure. The following discussion focuses on the cases with  $\text{O}_2$  vol% = 21% to represent the combustion in air. Additional experiments at  $\text{O}_2$  vol% = 15% and 40% were also carried out, and the observed species distributions were similar, so these results are not discussed further here.  $X_{\text{NH}_3}$  was varied up to 40% to retain a methane dominated flame chemistry in this study while still capturing the key ammonia induced effects under present conditions.

At  $\Phi = 0.9$ , increasing  $X_{\text{NH}_3}$  can result in considerable decreases in the intensities of carbon-containing chemiluminescent species  $\text{CH}^*$ ,  $\text{CO}_2^*$  and  $\text{C}_2^*$  at the flame front, as shown in Fig. 12 (a). These trends are reasonable because the carbon fraction in the fuel mixture decreases as  $X_{\text{NH}_3}$  increases. The  $\text{OH}^*$  intensity at the flame front likewise decreases with increasing  $X_{\text{NH}_3}$ , consistent with observations reported in the literature [35]. The general distribution of  $\text{NH}_2^*$  is similar to previous methane-ammonia flames, while its intensity increases slightly with  $X_{\text{NH}_3}$ . The intensity of  $\text{H}_2\text{O}$  at the

flame front can be seen to increase significantly with  $X_{\text{NH}_3}$ , evidencing promotion of  $\text{H}_2\text{O}$  production by ammonia addition.

At  $\Phi = 1.2$ ,  $\text{OH}^*$  intensity continues to decrease with increasing  $X_{\text{NH}_3}$  at both the primary and secondary fronts, which is consistent with previous observations for methane-ammonia and hydrogen-ammonia flames [35,52]. Among the carbon-containing radicals,  $\text{CH}^*$ , and especially  $\text{C}_2^*$ , show marked decreases as  $X_{\text{NH}_3}$  increases, as shown in Fig. 12 (b). In contrast,  $\text{CO}_2^*$  exhibits a comparatively smaller decrease. This pattern suggests that the hydrocarbon reaction pathways in the primary stage under fuel-rich conditions are more sensitive to the involvement of  $\text{NH}_3$  or nitrogen-containing species than the final oxidation process to  $\text{CO}_2$ . Meanwhile, both the intensity of  $\text{NH}_2^*$  and the spatial extent of  $\text{NH}_2^*$ -characterised intermediate region increase with  $X_{\text{NH}_3}$ , further supporting the notion that this region is strongly related to the low reactivity of ammonia. Additionally, the effect of  $X_{\text{NH}_3}$  on  $\text{H}_2\text{O}$  is concentrated at the primary flame front, where the  $\text{H}_2\text{O}$  intensity increases with  $X_{\text{NH}_3}$ , whereas it is comparatively unaffected at the secondary flame front. Overall, these trends indicate that  $\text{NH}_3$  mainly enhances  $\text{H}_2\text{O}$  formation in the fuel-rich primary combustion process rather than in the secondary combustion process across the investigated  $X_{\text{NH}_3}$  range.

Meanwhile, the species distributions under varying  $X_{\text{NH}_3}$  are generally consistent with the previous fuel-rich cases, as shown in Fig. 12 (b). In particular,  $\text{CH}^*$  and  $\text{C}_2^*$  are absent at the secondary flame front and confined to the primary flame front, whereas the secondary flame front is dominated by  $\text{OH}^*$  and  $\text{CO}_2^*$  with only a weak  $\text{NH}_2^*$  contribution. This is also supported by the emission spectrum at the secondary flame front for  $X_{\text{NH}_3} = 0.4$  (point C, Fig. 12 (c)), which shows no discernible  $\text{CH}^*$  and  $\text{C}_2^*$  peaks, and a much weaker  $\text{NH}_2^*$  continuum than at primary front (point A, Fig. 12 (c)) and in the intermediate region (point B, Fig. 12 (c)). Meanwhile,  $\text{CO}_2^*$  continuum is relatively stronger at point C, shifting the broadband maximum towards around 400–500 nm instead of the 600–700 nm associated with  $\text{NH}_2^*$  emission. Therefore, within the investigated  $X_{\text{NH}_3}$  range, these observations indicate that increasing  $X_{\text{NH}_3}$  does not change the key secondary-front chemistry, and hydrocarbon-related excited radicals remain negligible at the secondary flame front.

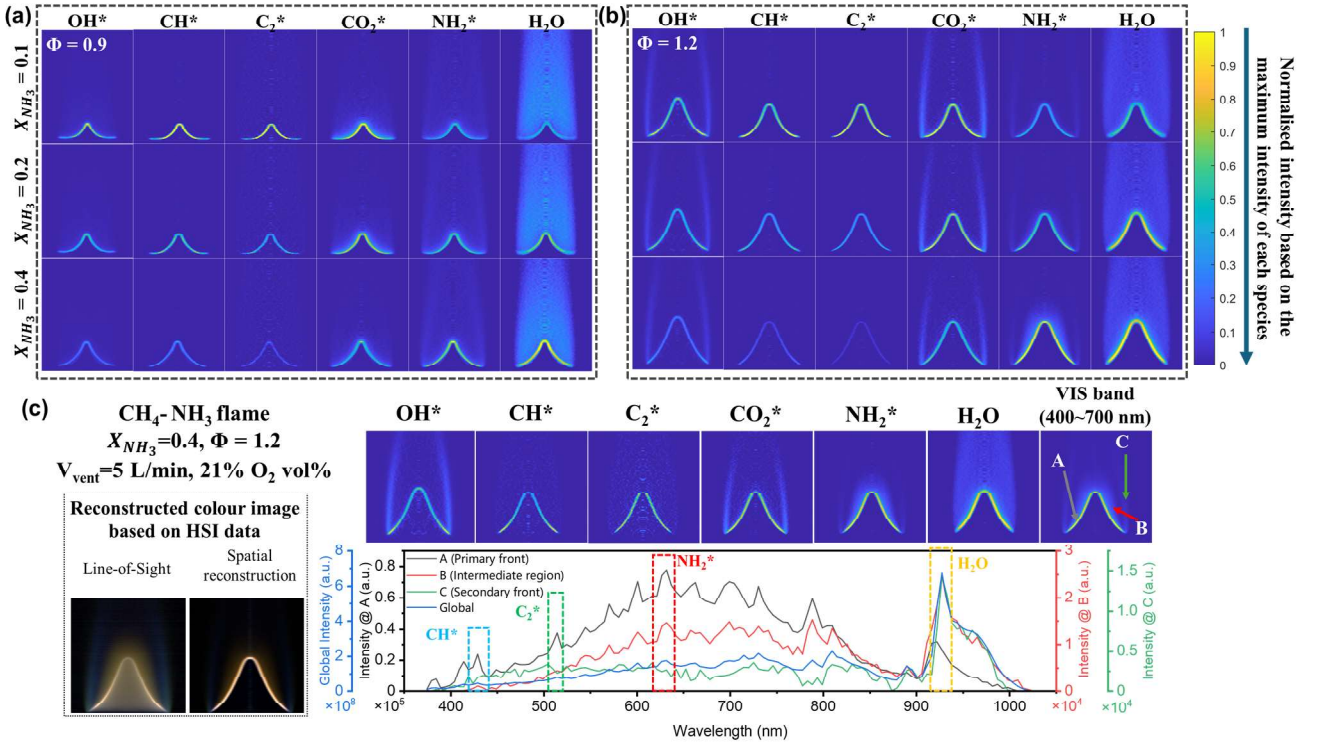


Fig. 12 Comparison of key species spatial distributions in the  $\text{CH}_4\text{-NH}_3$  flame with varying with  $X_{\text{NH}_3}$  under ventilation with 21%  $\text{O}_2$  vol% at (a)  $\Phi = 0.9$  and (b)  $1.2$ . (c) Reconstruction results and corresponding spectra at different locations for  $\text{CH}_4\text{-NH}_3$  flame of  $\Phi = 1.2$ ,  $X_{\text{NH}_3} = 0.4$ ,  $\dot{V}_{\text{vent}} = 5$  L/min.

### 3.2.3. Summaries from the flame reconstruction results

Based on the species spatial distributions and the emission spectra, several features of the primary and secondary combustion can be elucidated. In fuel-rich premixed methane flames, the UV-VIS emission from the primary flame front is dominated by OH\*, CH\*, C<sub>2</sub>\* and CO<sub>2</sub>\*, and in methane-ammonia flames, NH<sub>2</sub>\* also contributes. This suggests that the primary combustion process involves the oxidation of hydrocarbon species and ammonia. At the secondary flame front in both fuel-rich premixed methane and methane-ammonia flame, UV-VIS emission is predominantly contributed by OH\* and CO<sub>2</sub>\*, with CH\* and C<sub>2</sub>\* being notably absent. The visible bluish luminosity of the secondary front is therefore largely attributable to CO<sub>2</sub>\*. Together with the presence of H<sub>2</sub>O at the secondary flame front, these signatures suggest that the secondary combustion is governed mainly by oxidation of H<sub>2</sub> and moist CO rather than by hydrocarbon pathways, within the investigated conditions up to a X<sub>NH<sub>3</sub></sub> of 0.4. Because their oxidation pathways involve the production of OH\* and CO<sub>2</sub>\* instead of CH\* and C<sub>2</sub>\* [53,54]. These observations also imply that OH\* formation follows different dominant routes in the primary and secondary combustion process. The result also corroborates inferences from PMT measurements for methane flames under oxygen-rich conditions, namely the increase of global OH\* with  $\Phi$  in the fuel-rich range is driven by the strengthening of OH\* at the secondary front. It also explains the more luminous yet less saturated flame appearance, attributable to enhanced CO<sub>2</sub>\* continuum emission.

### 3.3. Kinetic calculations

To clarify the mechanism of the secondary combustion in fuel-rich methane and methane-ammonia flames, one dimensional kinetic calculation was performed at  $\Phi = 1.2$ , X<sub>NH<sub>3</sub></sub> = 0, 0.2 and 0.4, with the oxidiser stream O<sub>2</sub> vol% being 0%, 21% and 40% respectively.

#### 3.3.1. Methane flame

For methane flame at  $\Phi = 1.2$ , the results of 0% O<sub>2</sub> vol% are shown in Fig. 13. The temperature, heat release and species profiles show a single sharp change near 0.4 cm and no secondary peak within the calculation domain. A weak secondary feature present in the rate of production (ROP) of H<sub>2</sub>, CO, H<sub>2</sub>O and CO<sub>2</sub> present between 1.2 and 1.3 cm as shown in Fig. 13 (c). This behaviour arises from decomposition of H<sub>2</sub>O via the reverse reaction of OH + H<sub>2</sub> ↔ H + H<sub>2</sub>O, which generates OH and H<sub>2</sub>. The resulting OH subsequently oxidises CO via OH + CO ↔ H + CO<sub>2</sub>. Thus, slow secondary reactions of CO and H<sub>2</sub> can proceed in oxygen-free environment, but at rates far below those at flame front.

At 21% and 40% O<sub>2</sub> vol%, the heat release and temperature profiles exhibit a secondary rising at about 1.1 ~ 1.2 cm after the primary peak, as shown in Fig. 13 (b), indicating secondary combustion. Meanwhile, the secondary increases in both heat release and temperature are significantly lower than the primary increases, indicating that most heat is released in the primary premixed combustion process. Consistent with these profiles, OH\* and CO<sub>2</sub>\* show two distinct peaks, one aligned with the primary heat release peak and a second at about 1.1–1.2 cm aligned with the secondary peak, as shown in Fig. 13 (a). By contrast, CH\* and C<sub>2</sub>\* each show a single peak at primary flame front and remain absent at the secondary front. These trends match the flame reconstructions, which confirms that reactions associating with OH\* and CO<sub>2</sub>\* production dominate the secondary combustion process, rather than those of CH\* and C<sub>2</sub>\*.

The secondary peak location of heat release, OH\* and CO<sub>2</sub>\* also correspond to the location that the mole fractions of CO and H<sub>2</sub> decreases rapidly to negligible levels. The results of ROP shown in Fig. 13 (c) show that this CO and H<sub>2</sub> consumption is accompanied by CO<sub>2</sub> and H<sub>2</sub>O formation at the same locations, indicating that CO and H<sub>2</sub> are the main reactants in the secondary combustion process.

Furthermore, it can be found that CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, and CH<sub>3</sub>OH, taken here as representative hydrocarbon species, show noticeable ROP variations only near 0.4 cm. C<sub>2</sub>H<sub>2</sub> and CH<sub>3</sub>OH are consumed immediately after formation, and no comparable ROP changes are observed between 0.9 and 1.4 cm, as shown in Fig. 13 (d). This means that the hydrocarbon-related reactions are concentrated in the primary combustion and remain negligible in secondary combustion region.

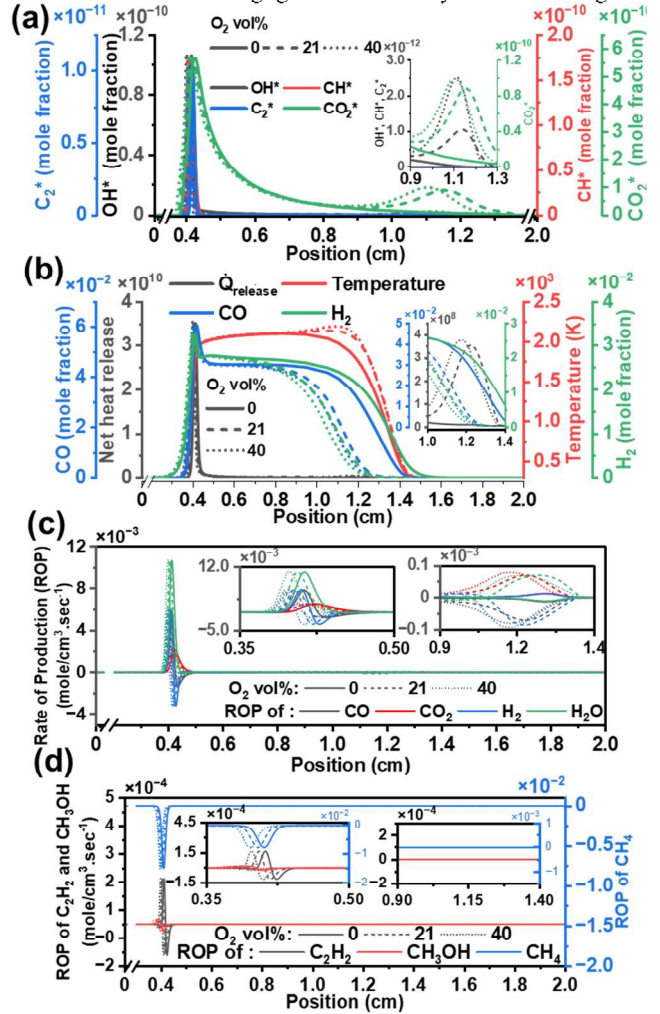


Fig. 13 Distributions of the key parameters from the kinetic calculation in CH<sub>4</sub> combustion with  $\Phi = 1.2$  under varying O<sub>2</sub> vol%.

The ROP analysis (Fig. 14 (a) and (b)) at the secondary heat release peak confirms that H<sub>2</sub>O is mainly produced and H<sub>2</sub> is mainly consumed via the same reaction OH + H<sub>2</sub> ↔ H + H<sub>2</sub>O, with additional contributions from reactions of OH with H<sub>2</sub>, HO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub>. CO<sub>2</sub> is formed predominantly from CO consumption via OH + CO ↔ H + CO<sub>2</sub>, with only minor contributions from other pathways. Accordingly, OH plays a crucial role during the secondary combustion process, as it directly participates in the dominant CO and H<sub>2</sub> consumption routes. At the same location, OH is sustained by strong regeneration reactions, including the reverse reaction 2OH ↔ O + H<sub>2</sub>O and H + O<sub>2</sub> ↔ O + OH, which together maintain the radical pool during secondary combustion. Changing the O<sub>2</sub> vol% does not alter the dominant pathways but modulates their rates. Increasing O<sub>2</sub> vol% generally accelerates both H<sub>2</sub>O production and its decomposition, while OH + H<sub>2</sub> ↔ H + H<sub>2</sub>O exhibits a nonlinear dependence on O<sub>2</sub> vol%. The formation of CO<sub>2</sub> remains dominated by OH + CO ↔ H + CO<sub>2</sub> for all examined O<sub>2</sub> vol%. Consistently, Fig. 14 (c) demonstrates that OH\* production routes differ between the primary and secondary combustion process: CH + O<sub>2</sub> ↔ CO + OH\* dominates at the primary front, which is the key OH\* production pathways in hydrocarbon combustion process, while H + O + M ↔ OH\* + M dominates at the secondary front.

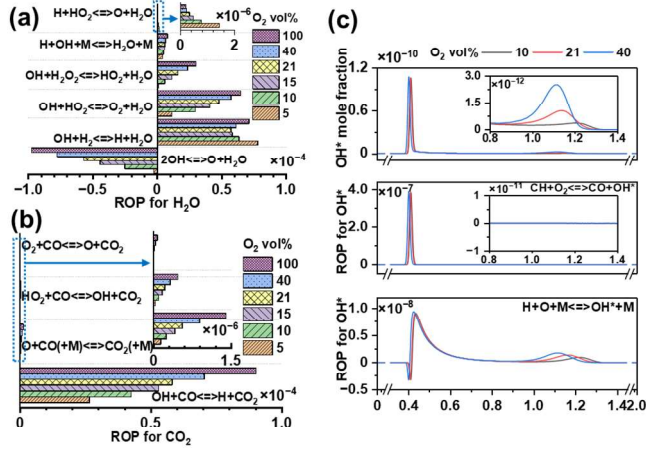


Fig. 14 ROP for (a) H<sub>2</sub>O and (b) CO<sub>2</sub> at the secondary flame front; (c) ROP of different routes for OH\* production in CH<sub>4</sub> combustion with  $\Phi = 1.2$  under varying O<sub>2</sub> vol%.

Overall, the chemistry of the secondary combustion closely resembles the H<sub>2</sub> and moist CO oxidation. Therefore, the secondary combustion process of methane is essentially the combustion of H<sub>2</sub> and moist CO, rather than the combustion of unburnt methane or other hydrocarbons.

### 3.3.2. Methane-ammonia flame

#### ➤ Effect of O<sub>2</sub> vol%

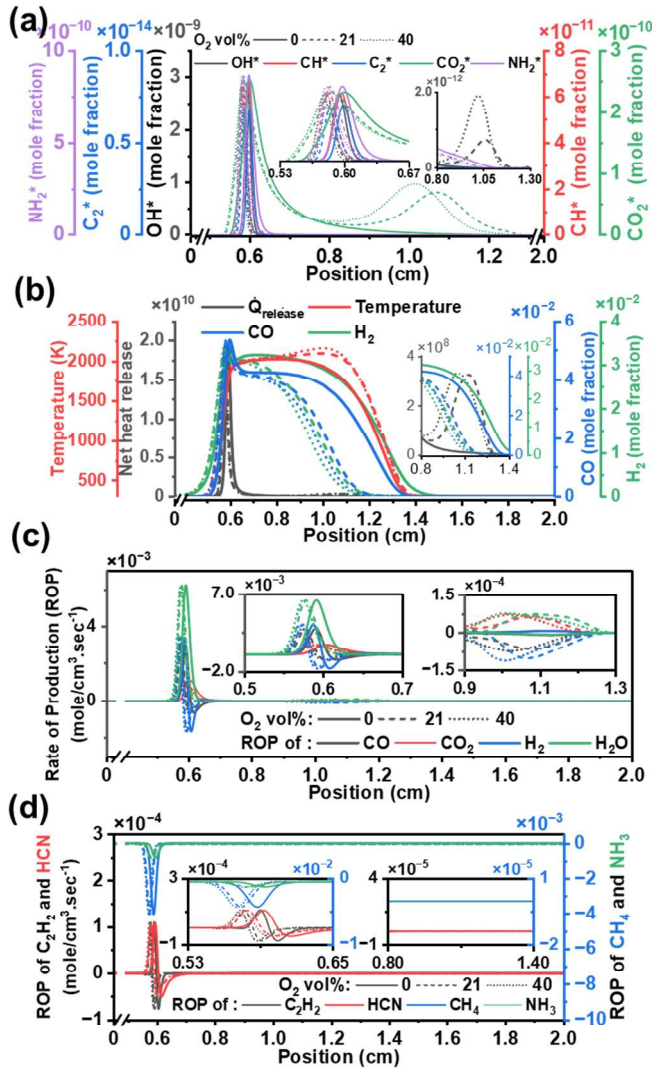


Fig. 15 Distributions of the key parameters from the kinetic calculation in CH<sub>4</sub>-NH<sub>3</sub> combustion with  $\Phi = 1.2$  under varying O<sub>2</sub> vol%.

For the ammonia-containing cases, the general profiles are similar to those of methane cases. Taking  $X_{\text{NH}_3} = 0.2$  as an example, at 0% O<sub>2</sub> vol%, no secondary heat release can be identified. Consistently, CH\*, C<sub>2</sub>\* and OH\* are confined to a narrow region around the primary flame front, whereas only trace amount of CO<sub>2</sub>\* and NH<sub>2</sub>\* persist downstream, in agreement with the flame reconstructions. Meanwhile, the primary flame front shifts toward the oxidiser side compared with the methane cases, to about 0.6 cm. Minor production of CO<sub>2</sub> and H<sub>2</sub> and consumption of CO and H<sub>2</sub>O can still be identified, via pathways same as methane cases, with a minor additional contribution from  $\text{HNO} + \text{H} \leftrightarrow \text{NO} + \text{H}_2$ .

At 21% and 40% O<sub>2</sub> vol%, a clear secondary combustion process appears, manifested by the secondary peaks in temperature, heat release, and OH\* and CO<sub>2</sub>\* profiles, as shown in Fig. 15 (a) and (b). CH\*, C<sub>2</sub>\* and NH<sub>2</sub>\* remain absent at the secondary front, consistent with both the experiments and the pure-methane results. The mole fractions of H<sub>2</sub> and CO decrease rapidly to near zero at similar locations, and their ROP profiles show clear valleys at the same location accompanied by CO<sub>2</sub> and H<sub>2</sub>O production, as shown in Fig. 15 (c). ROP of representative intermediates, including C<sub>2</sub>H and HCN, show formation and rapid consumption confined to the primary zone, without subsequent changes (Fig. 15 (d)). This reinforces that hydrocarbons and C–N species is largely confined to the primary combustion process under the present methane chemistry dominated conditions of  $X_{\text{NH}_3} = 0.2$ .

The ROP analysis at the secondary front shows that H<sub>2</sub>O is still produced mainly by  $\text{OH} + \text{H}_2 \leftrightarrow \text{H} + \text{H}_2\text{O}$  under both 21% and 40% O<sub>2</sub> vol%, as demonstrated in Fig. 16 (a). Compared with the methane case, this production route becomes stronger than competing decomposition and other production routes. The contribution of  $\text{H} + \text{OH} + \text{M} \leftrightarrow \text{H}_2\text{O} + \text{M}$  increases, while that of  $\text{OH} + \text{HO}_2 \leftrightarrow \text{H}_2\text{O} + \text{O}_2$  decreases. CO<sub>2</sub> formation remains dominated by CO oxidation via  $\text{OH} + \text{CO} \leftrightarrow \text{H} + \text{CO}_2$ , as shown in Fig. 16 (b). In addition, Fig. 16 (c) shows that the production pathways of OH\* at the primary and secondary flame fronts remain similar to methane cases, namely mainly through  $\text{CH} + \text{O}_2 \leftrightarrow \text{CO} + \text{OH}^*$  at the primary front, and  $\text{H} + \text{O} + \text{M} \leftrightarrow \text{OH}^* + \text{M}$  at the secondary front.

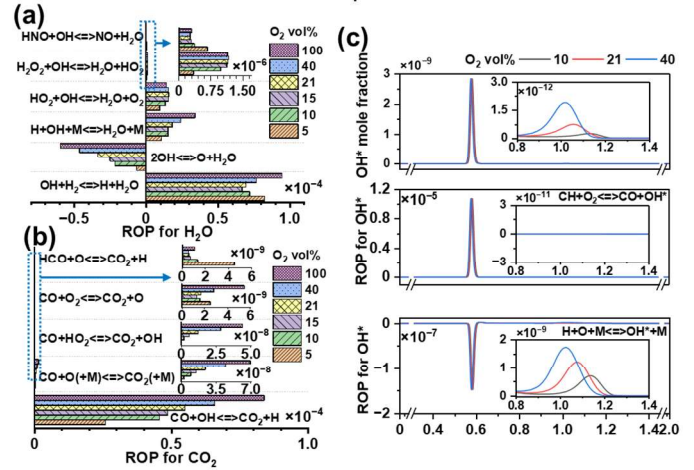


Fig. 16 ROP for (a) H<sub>2</sub>O and (b) CO<sub>2</sub> at the secondary flame front; (c) ROP of different routes for OH\* production in CH<sub>4</sub>-NH<sub>3</sub> combustion with  $\Phi = 1.2$  under varying O<sub>2</sub> vol%.

For clarity, the ROP results shown here list the highest-contributing reactions ranked by their contributions at the secondary front. Under this ranking, nitrogen-involving reactions do not appear among the dominant contributors. More generally, nitrogen-containing species, such as NO and NO<sub>2</sub>, can slightly modify the hydrocarbon oxidation pathways by affecting OH and H formation, for example via  $\text{NO}_2 + \text{H} \leftrightarrow \text{NO} + \text{OH}$ , but they do not change final oxidation process  $\text{CO} \rightarrow \text{CO}_2$  under the present conditions. Meanwhile, NO and NO<sub>2</sub> can proceed via HONO and HNO intermediates and thereby contribute to H<sub>2</sub>O formation through their influence on the OH production.

However, the contributions of nitrogen-involving reactions to OH and H production are on the order of  $10^{-7}$ , which remains much smaller than the order of  $10^{-4}$  associated with the CO and H<sub>2</sub> oxidation routes to OH and H production. This indicates that the secondary-front chemistry is controlled primarily by oxidation of CO and H<sub>2</sub> rather than both C-N compounds or nitrogen-containing species under present ammonia fraction.

Therefore, the current results suggest that the secondary combustion is still governed by the oxidation of CO and H<sub>2</sub> when ammonia is present at  $X_{\text{NH}_3} = 0.2$ .

#### ➤ Effect of $X_{\text{NH}_3}$

Varying  $X_{\text{NH}_3}$  can also result in changes in the profiles of focused parameters in both primary and secondary combustion processes. For consistency with the experimental condition, the discussion below refers to the oxidiser of 21% vol%, as shown in Fig. 17. Increasing  $X_{\text{NH}_3}$  can shift both flame fronts toward the stagnation plane owing to the reduced flame speed, decrease the mole fractions of OH\*, CH\*, C<sub>2</sub>\*, and CO<sub>2</sub>\* at the primary flame front, and increases the mole fractions of NH<sub>2</sub>\* and H<sub>2</sub>O owing to greater ammonia participation. The primary heat release decreases substantially with  $X_{\text{NH}_3}$ , whereas the secondary heat release is only weakly affected, as shown in Fig. 17 (b). In addition, CH\* and C<sub>2</sub>\* remains confined at primary front, while OH\* and CO<sub>2</sub>\* distribute at both primary and secondary front.

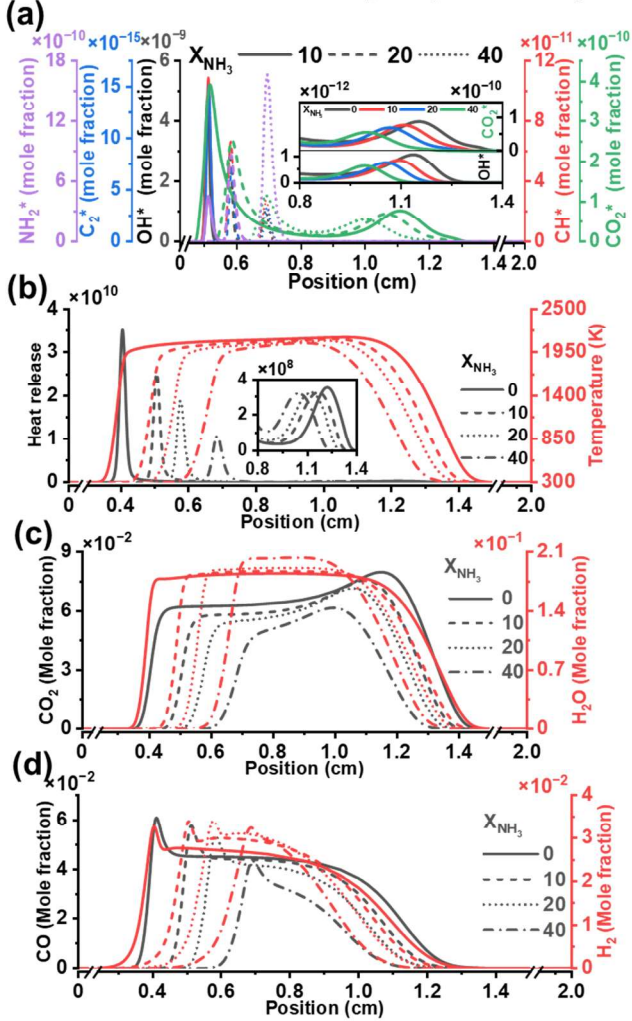


Fig. 17 Distributions of the key parameters from the kinetic calculation in CH<sub>4</sub>-NH<sub>3</sub> combustion with  $\Phi = 1.2$ , 21% O<sub>2</sub> vol%, under varying  $X_{\text{NH}_3}$ .

Furthermore, the mole fraction of CO<sub>2</sub> decreases with  $X_{\text{NH}_3}$ , as shown in Fig. 17 (c), in line with the decreases in CO peak mole fraction, as shown in Fig. 17 (d). In contrast, the peak H<sub>2</sub> mole fraction changes

only modestly as  $X_{\text{NH}_3}$  varies. A slight increase in H<sub>2</sub> mole fraction between the primary and secondary front can be found as ammonia being introduced, governed mainly by the reverse of  $\text{OH} + \text{H}_2 \leftrightarrow \text{H} + \text{H}_2\text{O}$ . Although this reverse reaction also occurs in the  $X_{\text{NH}_3} = 0$  case at the similar location, it does not lead to a noticeable H<sub>2</sub> mole fraction increase. This difference arises from the distinct oxidation route between NH<sub>3</sub> and CH<sub>4</sub>. Under fuel-rich condition, methane is primarily oxidised via  $\text{H} + \text{CH}_4 \leftrightarrow \text{CH}_3 + \text{H}_2$ , with partial contribution from  $\text{OH} + \text{CH}_4 \leftrightarrow \text{CH}_3 + \text{H}_2\text{O}$ . While, NH<sub>3</sub> is mainly oxidised via  $\text{NH}_3 + \text{OH} \leftrightarrow \text{NH}_2 + \text{H}_2\text{O}$ , and H and O attacking NH<sub>3</sub> are not less competitive except at very rich conditions [55]. Consequently, more H<sub>2</sub>O is produced at the primary front, which enhances the reverse of  $\text{OH} + \text{H}_2 \leftrightarrow \text{H} + \text{H}_2\text{O}$ , and yields a slightly higher H<sub>2</sub> level downstream. This also explains the more pronounced H<sub>2</sub>O concentration at the primary front observed experimentally.

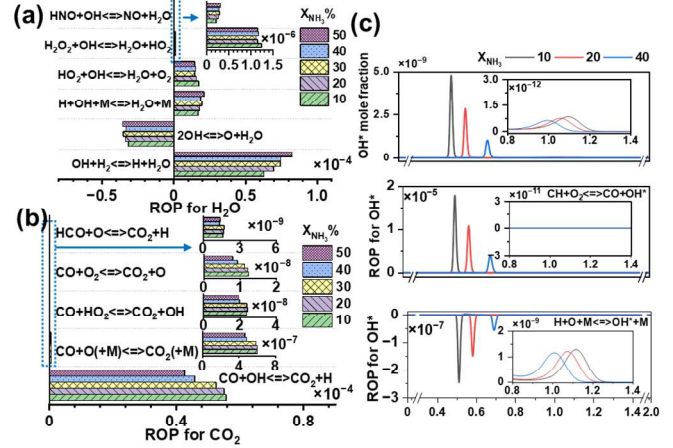


Fig. 18 ROP for (a) H<sub>2</sub>O and (b) CO<sub>2</sub> at the secondary flame front; (c) ROP of different routes for OH\* production in CH<sub>4</sub>-NH<sub>3</sub> combustion with  $\Phi = 1.2$ , 21% O<sub>2</sub> vol%, under varying  $X_{\text{NH}_3}$ .

The ROP analysis for H<sub>2</sub>O, CO<sub>2</sub> and OH\* at the secondary flame front (Fig. 18 (a) and (b)) shows that the production of CO<sub>2</sub> and H<sub>2</sub>O, and dominant OH\* production routes remain essentially unchanged when  $X_{\text{NH}_3}$  varies. Increasing  $X_{\text{NH}_3}$  slightly enhances  $\text{OH} + \text{H}_2 \leftrightarrow \text{H} + \text{H}_2\text{O}$  for H<sub>2</sub>O production and inhibits  $\text{OH} + \text{CO} \leftrightarrow \text{H} + \text{CO}_2$  for CO<sub>2</sub> production. The H<sub>2</sub>O decomposition pathway shows only limited changes, suggesting that the greater NH<sub>3</sub> participation essentially promotes H<sub>2</sub>O formation. Meanwhile, nitrogen-involving reactions remain minor contributors under the present conditions. Thus, higher ammonia fraction mainly promotes H<sub>2</sub>O formation without altering the central role of CO and H<sub>2</sub> oxidation in the secondary combustion under the methane chemistry dominated conditions of  $X_{\text{NH}_3}$  up to 0.4.

In summary, the results of kinetic calculations are generally consistent with the main experimental observations. In detail, CH\* and C<sub>2</sub>\* are restricted to the primary flame front because their dominant formation reactions involve hydrocarbon species that are only significant in the primary combustion process. In contrast, OH\* and CO<sub>2</sub>\* are produced both at the primary and secondary flame front, since both hydrocarbons oxidation and oxidation of H<sub>2</sub> and moist CO involve their production. Meanwhile, the calculations also corroborate the inference of distinct OH\* formation routes at the two flame fronts. Therefore, under the investigated conditions of  $X_{\text{NH}_3}$  up to 0.4, that the methane chemistry remains dominant, the results support the mechanistic interpretation of the secondary combustion process for methane and methane-ammonia flames that they are essentially the combustion of H<sub>2</sub> and moist CO, with barely any participation from hydrocarbons and C-N compounds.

## 4. Conclusions

This study experimentally investigates the flame structure and combustion characteristics of laminar fuel-rich methane and methane-ammonia flames with a focus on the characteristics of the secondary

combustion. Ammonia fractions up to  $X_{\text{NH}_3} = 0.4$  are considered, representing methane dominated ammonia blended mixtures within the scope of the present study. The general behaviours of the flame and its secondary combustion front are investigated based on flame images and the spectral features of global chemiluminescence. Subsequently, hyperspectral imaging combined with Tikhonov-regularisation based reconstruction is utilised for the spatial and spectral reconstruction of the distributions of  $\text{OH}^*$ ,  $\text{CH}^*$ ,  $\text{C}_2^*$ ,  $\text{CO}_2^*$ ,  $\text{NH}_2^*$  and  $\text{H}_2\text{O}$  based on their spontaneous emission/radiation, and thus enabling analysis of the flame structure and the combustion behaviour at both primary and secondary flame fronts. Finally, simplified kinetic calculations were performed and the dominant reaction features and participation species in the secondary combustion of methane and methane-ammonia flames were revealed. Current results can deepen our understanding of secondary combustion in methane and methane-ammonia flames and can potentially provide insights into the optimisation and control of Rich–Quench–Lean (RQL) combustion using methane and ammonia-containing low-carbon fuels. The main conclusions are summarised as follows:

1. The shape of the secondary flame front of a fuel-rich laminar methane and methane-ammonia flame closely resembles the Burke-Schumann diffusion flame. When air is used as the ventilating stream, under- and over-ventilated conditions can be identified, and this classification applies consistently to both the secondary flame front shape and the global chemiluminescence intensities. When the  $\text{O}_2$  vol% of the ventilating stream is varied, this classification no longer holds; instead, both the secondary front shape and the global chemiluminescence intensities increase approximately monotonically with  $\text{O}_2$  vol%.
2. For both methane and methane-ammonia flames, emissions at the secondary flame front are dominated by  $\text{OH}^*$  and  $\text{CO}_2^*$ , whereas  $\text{CH}^*$  and  $\text{C}_2^*$  are solely confined to the primary flame front. In the visible band, the secondary front luminosity of both fuels is governed primarily by  $\text{CO}_2^*$ . For methane-ammonia flames,  $\text{NH}_2^*$  contributes at the primary flame front and the intermediate region between two the flame fronts, but remains weak at the secondary front. With the increasing ammonia fraction,  $\text{OH}^*$ ,  $\text{CH}^*$ ,  $\text{C}_2^*$  and  $\text{CO}_2^*$  decrease while  $\text{NH}_2^*$  increases, and  $\text{H}_2\text{O}$  production is enhanced at the primary front.
3. The secondary combustion in both methane and methane-ammonia flames is essentially governed by the oxidation of moist CO and  $\text{H}_2$ , with only limited involvement of hydrocarbons and C–N compounds over the investigated ammonia-fraction range. Consistent with this, the dominant  $\text{OH}^*$  formation route differs at the two flame fronts:  $\text{CH} + \text{O}_2 \rightarrow \text{CO} + \text{OH}^*$  at the primary front, whereas  $\text{H} + \text{O} + \text{M} \rightarrow \text{OH}^* + \text{M}$  at the secondary front. Variation of  $\text{O}_2$  vol% and ammonia fraction mainly modulates the rates rather than the pathways for  $\text{CO}_2$  and  $\text{H}_2\text{O}$  production during the secondary combustion process for both fuels.

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